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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	October 20, 1993	Interim January 1, 1991–October 31, 1993

4. TITLE AND SUBTITLE
Dynamics of Adsorbed, Swollen Block Copolymers

5. FUNDING NUMBERS
PE-N0014-91-J-1274
PR-1274

2

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8. PERFORMING ORGANIZATION REPORT NUMBER
UMR-FDB- 32

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10. SPONSORING/MONITORING AGENCY REPORT NUMBER

DTIC
ELECTE
NOV 03 1993
S D
A

11. SUPPLEMENTARY NOTES
For Publication in Macromolecules

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Unlimited - Approved for unlimited plubic release

12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

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14. SUBJECT TERMS	15. NUMBER OF PAGES
Block Copolymers, dynamics, NMR spectroscopy	24
	16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
Unclassified	Unclassified	Unclassified	

Best Available Copy

OFFICE OF NAVAL RESEARCH

Grant N00014-91-J-1274

R&T Code 413m005---04

Technical Report # UMR-FDB-32

Dynamics of Adsorbed, Swollen Block Copolymers

by

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Prepared for Publication in

Macromolecules

October 20, 1993

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Abstract

Deuterium NMR relaxation times of specifically deuterated block terpolymers of 2-vinyl pyridine (VP), styrene (S), and deuterostyrene (DS) were measured for the polymers in solution and on silica as a function of temperature and solvent. The block polymers were attached to the silica through the VP segments; the S and DS segments were extended into the solution. In a thermodynamically poor solvent, such as carbon tetrachloride, the relaxation times were consistent with the S segments on the surface-bound polymer being less mobile than their counterparts in solution. This is in contrast with their behavior in toluene (previously reported), where the styrene segments of the surface-bound polymer appeared to be more mobile than in solution. The results demonstrate that the solvent quality may have a dramatic effect on the dynamics of the chain segments of the surface-bound polymer. In a mixture of solvents, namely carbon tetrachloride and methanol there was evidence for more mobile S segments in the surface-bound polymer, however, the VP units also had additional mobility due to the presence of the methanol. The relaxation times were also used, along with the model of Hall and Helfand, to determine the motional parameters and spectral densities for the polymers in the different systems.

Introduction

The dynamics and conformation of polymers adsorbed on inorganic substrates and swollen with solvents is of importance in many commercial applications such as coatings, adhesives, chromatography, etc. [1] One of the major applications of polymers adsorbed on surfaces is in the stabilization of colloidal dispersions. Stabilization can be achieved through entropic means where extended polymer chains avoid each other due to the decreased entropy associated with chain overlap. Numerous approaches have been proposed to describe the conformation of adsorbed polymers [2-6] on solid substrates. These studies report attempts to model the polymers adsorbed on surfaces and predict their conformation when attached. Much less effort has been applied in the characterization of the *dynamics* of the adsorbed chains.

Specifically-tailored block copolymers, rather than homopolymers, may be much more effective in applications requiring the polymeric stabilization of particles. These can be adsorbed from solvent systems where one block adsorbs on the particle and the other block remains extended, possibly even *superextended, into the solvent. Such species have been dubbed* polymer brushes and studies on these have been reviewed by Milner [7]. An example of one system capable of forming polymer brushes is the block copolymer of styrene (S) and 2-vinylpyridine (VP).

Several groups have studied the behavior of poly(2-vinylpyridine-co-styrene) (VPS) block copolymers and their interactions with the solid surfaces [8-16]. Hadziioannou et al. [8] measured the forces between VPS coated mica surfaces and postulated that the VP groups were absorbed and the styrene segments extended into solution. NMR studies by Blum et al. [9] have shown that in VPS on silica and swollen with toluene, the VP groups are rigid while the S groups are very mobile. Tsai et al. [10] have used surface enhanced Raman scattering to confirm that when VPS is adsorbed onto a silver surface, the VP block adsorbs more strongly than the styrene block. They also concluded that the VP block adsorbs with the formation of a σ-bond involving the pyridine nitrogen atom. The styrene segments were essentially absent from the interface.

The structure of the extended styrene chains in surface-bound VPS has also received some attention. From the surface force measurements [8], it was concluded that the onset of repulsive forces occur at about about 5 times the normal radius of gyration (R_g) for the styrene segments. NMR measurements on similar polymers [9] were consistent with extensions of 4 times R_g. The difference can be qualitatively accounted for by considering that the NMR measurements were sensitive to the average chain extension, while the onset of repulsive forces would be sensitive to the chains with the longest extensions. Brush layer thickness for VPS on mica was also estimated from reductions in flow in surface-treated mica membranes [11]. Neutron reflectivity [12] experiments also have been used to estimate brush thicknesses. The latter experiments and NMR [9] experiments were both consistent with a parabolic brush profile, such as that proposed by Milner et al. [6], although this is far from well established at this time.

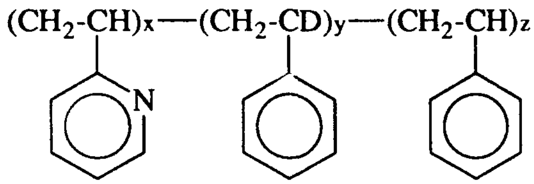
The adsorption of VPS on surfaces is dependent on a number of variables. Adsorption and X-ray photoelectron studies [13] were used to determine how the surface density depended on the copolymer block size asymmetry ratio. Two regimes were found where the adsorption density depended on the molecular weight of either component depending on the value of the asymmetry ratio. Huguenard et al. [14] have studied the adsorption of these species with radio-labelled polymers below their critical micelle concentration (CMC). They observed an initial fast adsorption of the VP segments followed a slower rearrangement. Using surface plasmons, the adsorption process has been shown to follow other than first-order kinetics [15]. Estimates of the chain extension of the styrene segments were also made. Very recently, surface force measurements [16] have been used to show that lower molecular weight VPS polymers actually displace higher molecular weight ones on mica, in contrast to the accepted behavior for homopolymers. Clearly these absorbed polymers have interesting, possibly unique, properties.

In our previous work [9], we reported results on the structure and dynamics of VPS polymers on silica, swollen with toluene. The two VPS block polymers were specifically deuterated at the methine position in continuous styrene segments, namely, poly(2-vinylpyridine-co-styrene-co-deuteriostyrene) (VPSDS) and poly(2-vinylpyridine-co-deuteriostyrene-co-styrene)

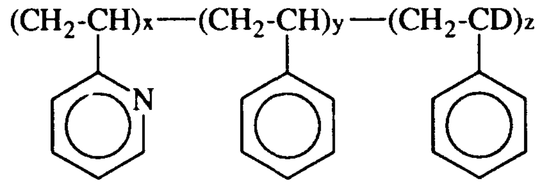
(VPDSS). As mentioned above, this study allowed us to estimate the extension of the styrene brushes in the toluene dispersion. In addition, a comparison of the deuterium NMR relaxation times of the swollen surface polymer with the solution polymer revealed that the local segmental dynamics of the polymer may actually be *faster* than that in a solution of similar concentration. In this paper, we report our work on the dynamics and structure of these polymers adsorbed on silica and swollen with CCl_4 and CCl_4/CH_3OH mixture. The aim is to extend our understanding of the polymer dynamics to thermodynamically poorer solvent systems. Deuterium NMR relaxation times (T_1 and T_2) of the deuterated styrene blocks in the adsorbed polymers have been used along with the Hall-Helfand (HH) model [17] to interpret the NMR relaxation time data in terms of the rates of molecular motion.

Experimental

The synthesis, characterization, and chemical structures of the triblock terpolymers and other polymers used in this study have been reported earlier [9]. Basically they consist of *co-* or *ter-*polymers of 2-vinylpyridine (VP), styrene (S) and deuterostyrene (DS) where the deuteron was specifically labelled in the methine position. The terpolymer structures were:



VPDSS



VPSDS

with approximately 25% VP, 37.5% DS (or S), and 37.5% S (or DS) (M_w ~ 20 000 g/mol, polydispersities 1.4 - 1.5). A fully protonated copolymer, VPS-7 (MW ~ 20 000 g/mol, 25% VP-75% S), and methine deuterated polystyrene, DS (M_w = 265 500 g/mol), were also used. High surface area amorphous fumed silica, Cab-O-Sil, M-5 (Cabot Corporation, Tuscola, IL) with a nominal surface area of 200 ± 25 m^2/g provided the adsorption surface. The adsorption isotherms for VPS on silica were determined by mass difference and described previously [9].

The NMR measurements were made at three different temperatures on a Varian VXR-200 NMR spectrometer operating at 30.7 MHz for ^2H and 50.3 MHz for ^{13}C. Modulated proton decoupling was used in the ^{13}C experiment to completely decouple the proton from the carbons. Solutions of deuterostyrene (DS) and VPDSS in CCl_4 and CCl_4/CH_3OH mixture of several different concentrations were prepared along with samples with monolayer coverage of both the terpolymers. The samples with monolayer coverage of the terpolymers were prepared in toluene, washed with toluene, dried in a vacuum oven and reswollen with CCl_4 and CCl_4/CH_3OH mixture (9:1 by weight). The solvents were degassed before use. Deuterium relaxation times (T_1 and T_2) were measured for the methine deuteron. The T_1 values were measured using the inversionrecovery method (180°-t-90°) and the T_2's with the CPMG method [18]. A pulse delay of 410 ms (greater than 5 x T_1) was allowed for the deuterons to achieve equilibrium magnetization after each data acquisition. Typically 2000 (surface) and 200 (solution) transients were taken for each time value of the relaxation measurements. The errors in the relaxation time measurements were estimated to be about 3% for T_1 and about 10% for T_2.

Results

The adsorption isotherm for the fully protonated copolymer VPS-7 adsorbed from two solvents, CCl_4 and toluene, is shown in Figure 1. The plateau values for the copolymer adsorbed from toluene and CCl_4 were found to be 320 mg VPS-7/g silica and 300 mg VPS-7/g silica, respectively. The adsorption isotherm is not of the high affinity type probably because of its lower molecular weight and moderate polydispersities. However, the plateau values for VPS-7 in CCl_4 and toluene are quite similar. Consequently, we do not expect any significant changes in the amount of surface-bound polymers when the change from toluene to carbon tetrachloride is made.

<Figure 1>

In order to understand the dynamics in the CCl_4 adsorbed polymer system, we have chosen to compare the relaxation times to those of the DS polymer in solution. Shown in Figure 2 are the deuterium NMR relaxation time (T_1 and T_2) values for methine-labelled polystyrene (DS) at 13, 28, and 40 °C. The concentrations chosen were such that they would bracket the T_1 behavior of the surface-bound VPDSD polymer in the same solvent at the same temperature. Such an approach worked well in our previous work with the polymers dispersed in toluene [9]. In that system it did not matter whether the comparison was made with the terpolymer or homopolymer in solution. As expected, the relaxation times increase with increasing temperature and decreasing concentration. The values of T_1 are larger than T_2 as expected for polymers in solution [19].

<Figure 2>

The relaxation time results for the labelled segments of the two terpolymers (VPSDS and VPDSS) adsorbed on silica and reswollen with CCl_4 are given in Table I for the three temperatures. Also listed are the relaxation time values that the homopolymer (DS) solution would have at the same T_1 as that for the corresponding value of T_1 for VPDSS on the surface. These values are obtained by interpolation of the data in Figure 3. In addition, the relaxation parameters from the Hall-Helfand model (*vide infra*) are given.

<Table I>

The state of the surface-bound polymers swollen with solvent can be probed with conventional ^{13}C NMR. In good solvents for polystyrene (e.g. toluene and even CCl_4), the ^{13}C spectrum of the VPS on silica shows resolved resonances for the S segments and none for the VP segments--consistent with rigid VP and flexible S layers. Shown in Figure 3 is the proton-decoupled solution-state ^{13}C spectrum of VPS on silica swollen with a 9:1 mixture of CCl_4/CH_3OH. In contrast to the behavior in toluene [9], the mixed solvent system shows resolved resonances for VP at about 165, 150, 135, 120, and 115 ppm. These are indicative of the ability of the methanol to give motional freedom to VP and this provides evidence of the penetration of the methanol into the VP. It contrasts with toluene, where no mobility of the VP is detected by the NMR experiment.

<Figure 3>

The deuterium NMR relaxation times for the VPDSS polymer in a solution of CCl_4/CH_3OH (9:1 by weight) are shown in Figure 4. This solvent mixture is reported to be a theta-solvent for polystyrene at 25°C [20]. However, we were unable to dissolve our DS polymer in the mixed solvent system. We therefore used VPDSS for comparison. *Unlike the other solvent systems* used, methanol is a good solvent for poly(2-vinyl pyridine). Shown in Table II are the relaxation time results for the VPDSS and VPSDS polymers on silica swollen in the mixed solvent system at 28 °C and 40 °C. The behavior found in this system is similar to that found in CCl_4 although all of the corresponding relaxation times are higher for the mixed-solvent system.

<Figure 4> <Table II>

Discussion

NMR has been shown to be useful in determining the structure and dynamics of polymers adsorbed on surfaces and a few reviews of this have been written [21-24] with one focussing on the use of isotope labelled species [24] at interfaces. The behavior of the block copolymers on surfaces can be aided with proper comparisons of relaxation times. Previous work has demonstrated that the relaxation times of surface-bound polymers are sensitive to the local environment/concentration [9,25,26]. Facchini and Legrand [25] observed two-component relaxation behavior of poly(ethylene oxide) (PEO) grafted on silica and swollen in benzene. The proton spin-spin relaxation was determined to be concentration dependent and representative of very anisotropic motion. Cosgrove and Ryan [26] used small angle neutron scattering data to predict the concentration dependent T_2 profile of PEO at the polystyrene latex/water interface. The results were in good agreement with the measured T_2 behavior.

A comparison of the corresponding relaxation times for VPDSS and VPSDS both on silica reveals shorter relaxation times for VPDSS. This is true for either solvent system at any of the temperatures studied. It is consistent with a more motionally restricted environment for styrene segments closer to the VP points of attachment to the surface. The differences between the corresponding T_1 and T_2 in either solvent system for the surface-bound polymers are significantly bigger than those observed in toluene [9]. This indicates that the motion of the styrene segments in these solvents is more restricted and/or locally more anisotropic than in toluene. This is because CCl_4 and CH_3OH are thermodynamically "poorer" solvents for polystyrene than toluene.

An empirical way to determine the thermodynamic "quality" of a solvent for a polymer is by comparing the solubility parameters (δ) of the polymer and the solvent. The solubility parameters for toluene, CCl_4, methanol, and polystyrene are 8.9, 8.6, 14.5 and 9.1 cal/cc, respectively [20]. Since the magnitude of the difference between the solubility parameter for CCl_4 and polystyrene is greater than the difference between toluene and polystyrene, CCl_4 can be considered to be a "poorer" solvent for PS than toluene. Methanol is indeed a poor solvent for PS.

A comparison of the relaxation times of the adsorbed polymers and those in solution indicates that the motion of the styrene segments in the bound state is similar to that in solution in each case. A comparison between the different solvent systems reveals that the relaxation times are typically longer for the mixed solvent system. Even though methanol is a poor solvent for the styrene part, the mobility it imparts to the VP part may be sufficient to make the S segments move slightly faster. Methanol, being a good solvent for VP could affect partial or complete desorption of the vinyl pyridine groups from the surface. This is consistent with the ^{13}C NMR results in Figure 3. If all the segments of the vinyl pyridine groups were displaced from the surface, then the resulting mixture would essentially be composed of silica particles immersed in a solution of VPSDS or VPDSS in CCl_4/CH_3OH mixture. Consequently, the surface and solution relaxation times would be the same for such a system. We therefore conclude that the polymer is still bound.

A comparison of the T_2 values of the adsorbed polymers with the solution ones, when each has the same T_1 value, was made in Table I. It can be seen that the T_2 values for the adsorbed polymers are significantly lower than the corresponding solution values. This is opposite to what we observed with toluene as a solvent [8]. Consequently, in CCl_4, the longer range motions are believed to be slower when the polymer is in the adsorbed state than when it is in solution. This is probably because of interference and overlap of the surface polymer segments in a more collapsed state than in toluene. A direct comparison for the mixed solvent state has not been made because of the solution state and surface state relaxation values did not overlap sufficiently. This is possibly due to either the VP groups being partially attached or a different solution structure in the mixed solvent system.

Another appropriate comparison between relaxation times for different systems of VPDSS and VPSDS is made in Table III. The ratio of the relaxation times T_1 and T_2 can be used as an indicator of the deviation of the data from the NMR fast, isotropic-motion limit where T_1 should equal T_2. The ratios for the DS polymer in either toluene or CCl_4 (not shown in table) are around 1.2-1.3. For the swollen polymers on silica in toluene [9], we found the value to be about 1.1 which is consistent with an extended, extremely mobile chain. In contrast, the ratios for the surface-bound chains in CCl_4 are 1.6 - 1.7, indicative of a much more motionally-restricted environment. For CCl_4/CH_3OH the ratios are 1.2 - 1.45, indicative of intermediate mobility. Thus, it appears that the extended, highly mobile chains only seem to occur only with a very good solvent for styrene, namely toluene. The surface bound chains appear to be in a more restricted environment in the presence of CCl_4 and CH_3OH.

At this point, it may be appropriate to comment on what is inferred, based on the NMR results, about the chain mobility. The NMR experiments are sensitive to local to medium range motions, typically not overall chain motions. If one were to adopt the blob model, the motions responsible for the relaxations would probably be those contained within the blob. Thus, even though the entire chain may be stretched and overall anisotropic, the local motions of the segments inside of a blob could be fairly isotropic over the NMR timescale.

It is also appropriate to make a more quantitative estimate of the motional behavior of the polymers. We have previously tested several models [27] proposed for the dynamics of polymers in solution based on NMR relaxation time data. For the present data, we have chosen to employ the Hall-Helfand model (HH) to quantify the dynamics of this system. The HH model appears to work well in the limit of the relaxation times T_1 and T_2 being nearly equal. The relaxation times for a deuterium nucleus attached to a carbon atom are dominated by electric quadrupole effects and are given by:

$$1/T_1 = (3\pi^2/20)(e^2qQ/h)^2\{J(\omega_0) + 4J(2\omega_0)\}$$

and

$$1/T_2 = (3\pi^2/40)(e^2qQ/h)^2\{3J(0) + 5J(\omega_0) + 2J(2\omega_0)\}$$

where the term e^2qQ/h is the quadrupole coupling constant in kHz and $J(\omega)$ is the spectral density at different frequencies with ω_0 being the Larmor frequency. From the solid-state deuterium NMR spectrum of bulk DS, the quadrupole coupling constant was determined to be equal to 165 kHz. According to the HH model, the spectral density is given by [27,28]:

$$J(\omega) = 2A(\omega)\ \{[\lambda_0 (\lambda_0 + 2\lambda_1) - \omega^2]^2 + [2\ (\lambda_0 + \lambda_1)\ \omega]^2\}^{-0.25}$$

where

$$A(\omega) = \cos\{0.5\ \tan^{-1}[(2(\lambda_0 + \lambda_1)\omega)/(\lambda_0(\lambda_0 + 2\lambda_1) - \omega^2)]\}$$

λ_0 and λ_1 are the two fitted model parameters which have the units of rate. These two parameters represent the fast (short range) motions and slow (long range) motions of the polymer chain.

The motional parameters (λ_1 and λ_0) and the spectral density functions (J(0), J(ω_0) and J($2\omega_0$)) were calculated and compared to values obtained in solution for similar T_1 values. These are tabulated in Table I and II. The results clearly indicate the presence of slower motions of the polymer in the adsorbed state for CCl_4. This can be inferred by comparison of the J(0), or λ_0, values of the VPDSS polymers on surface and in solution. A similar comparison has not been done for VPSDS polymer because T_1 values of this polymer on the surface are much higher than those on solution. However, the spectral densities and HH parameters can be compared with the other systems. The differences in dynamics between adsorbed polymers in the two solvents appear to be that the slower motions in CCl_4 are more dominant (greater intensity) than in CCl_4/CH_3OH. This is observed in the values of J(0) or λ_0, with ether of these parameters being dominated mainly by the value of T_2. Larger increases in λ_0 are found for the VPSDS polymer in the mixed solvent, where the polymer appears to have more mobility further away from the surface than in carbon tetrachloride. This may be due to the partial release of the VP groups as previously mentioned.

As the temperature is increased from 13 to 40 °C, one sees (from Table I) that there is a decrease in the difference between the T_2 values of adsorbed VPDSS polymer and the T_2 value of solution for similar T_1 values. This is due to the increased motion of the polymer segments at higher temperature and better solvent quality. One might speculate that with increased solvent quality the behavior might approach that previously reported for toluene [9].

Conclusions

Information on the dynamics, and consequently, structure of terminally-attached block copolymers can be obtained from relaxation time measurements of specifically labelled polymers. The adsorbed polymers, swollen with a solvent, have been shown to behave differently from that in solution. For terminally attached VPS, the styrene segments appear to be more mobile and extended when swollen with toluene than in solution at similar concentrations. However, when swollen with carbon tetrachloride (a "poorer" solvent than toluene for the styrene block) the chains are more motionallv restricted than in solution--consistent with the notion that the chains are not highly extended. In a CCl_4/CH_3OH mixture, the VP segments appear to partially desorb from the substrate, but the chains are not completely removed. The mobility of the styrene segments in this mixed solvent system are also more restricted than in solution--also indicative of chains which are not highly extended. If our results are generalizable, the highly extended chains with extreme flexibility may only occur with solvents which are thermodynamically very good (i.e. styrene/toluene).

Acknowledgements

The authors thank the United States Office of Naval Research for its financial support of this project. The authors also thank Robert D. O'Connor for assisting with some of the calculations.

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Table I.

Relaxation Times, HH Parameters, and Spectral Densities for VPDSS and VPSDS Adsorbed on Silica and Swollen with CCl_4 and DS in CCl_4 Solution.

	T_1(ms)	T_2(ms)	$\lambda_1(10^9 s^{-1})$	$\lambda_0(10^7 s^{-1})$	J(0)[a]	$J(\omega_o)$[a]	$J(2\omega_o)$[a]
13 °C							
VPDSS (surface)	2.91	1.61	1.04	6.67	5.27	2.38	1.54
DS (solution)[b]	2.91	2.18	1.10	20.5	2.84	2.22	1.58
VPSDS (surface)	3.07	1.82	1.21	8.35	4.37	2.24	1.46
28 °C							
VPDSS(surface)	3.17	2.09	1.36	12.1	3.41	2.14	1.42
DS (solution)[b]	3.17	2.50	1.31	24.9	2.36	1.96	1.47
VPSDS (surface)	3.76	2.37	1.96	9.84	3.17	1.80	1.20
40 °C							
VPDSS(surface)	3.61	2.43	1.83	12.7	2.88	1.86	1.25
DS(solution)[b]	3.61	2.74	1.83	20.5	2.24	1.76	1.28
VPSDS (surface)	4.05	2.88	2.38	15.4	2.29	1.62	1.13

[a] - units of 10^{-9}s

[b] - interpolated - at the same T_1 value from Figure 3.

Table II.

Relaxation Times, HH Parameters, and Spectral Densities for VPDSS and VPSDS Adsorbed on Silica and Swollen with CCl_4/CH_3OH (9/1).

	T_1(ms)	T_2(ms)	$\lambda_1(10^9 s^{-1})$	$\lambda_0(10^7 s^{-1})$	$J(0)^a$	$J(\omega_0)^a$	$J(2\omega_0)^a$
28 °C							
VPDSS(surface)	3.21	2.30	1.42	16.7	2.83	2.05	1.42
VPSDS (surface)	4.03	3.37	2.13	31.2	1.67	1.47	1.17
40 °C							
VPDSS(surface)	3.82	2.82	2.10	18.1	2.24	1.69	1.20
VPSDS (surface)	4.68	3.90	3.02	30.0	1.45	1.27	1.00

[a] - units of 10^{-9}s

Table III.

Comparison of Relaxation Times T_1 and T_2 for Different Solvent Systems of Adsorbed on Silica and Solution VPDSS and VPSDS at 18 °C

System	T_1(ms)	T_2(ms)	T_1/T_2
VPDSS			
toluene(surface)[a]	3.63	3.38	1.07
toluene(solution)[a]	3.63	2.75	1.32
CCl_4(surface)[b]	3.05	1.80	1.69
CCl_4 /CH_3OH(surface)[b]	2.66	1.83	1.45
VPSDS			
toluene(surface)[a]	3.94	3.60	1.09
toluene(solution)[a]	3.94	3.25	1.21
CCl_4(surface)[b]	3.30	2.02	1.63
CCl_4 /CH_3OH(surface)[b]	3.44	2.89	1.19

[a] - from reference 9.

[b] - interpolated to 18 °C from temperature dependent data.

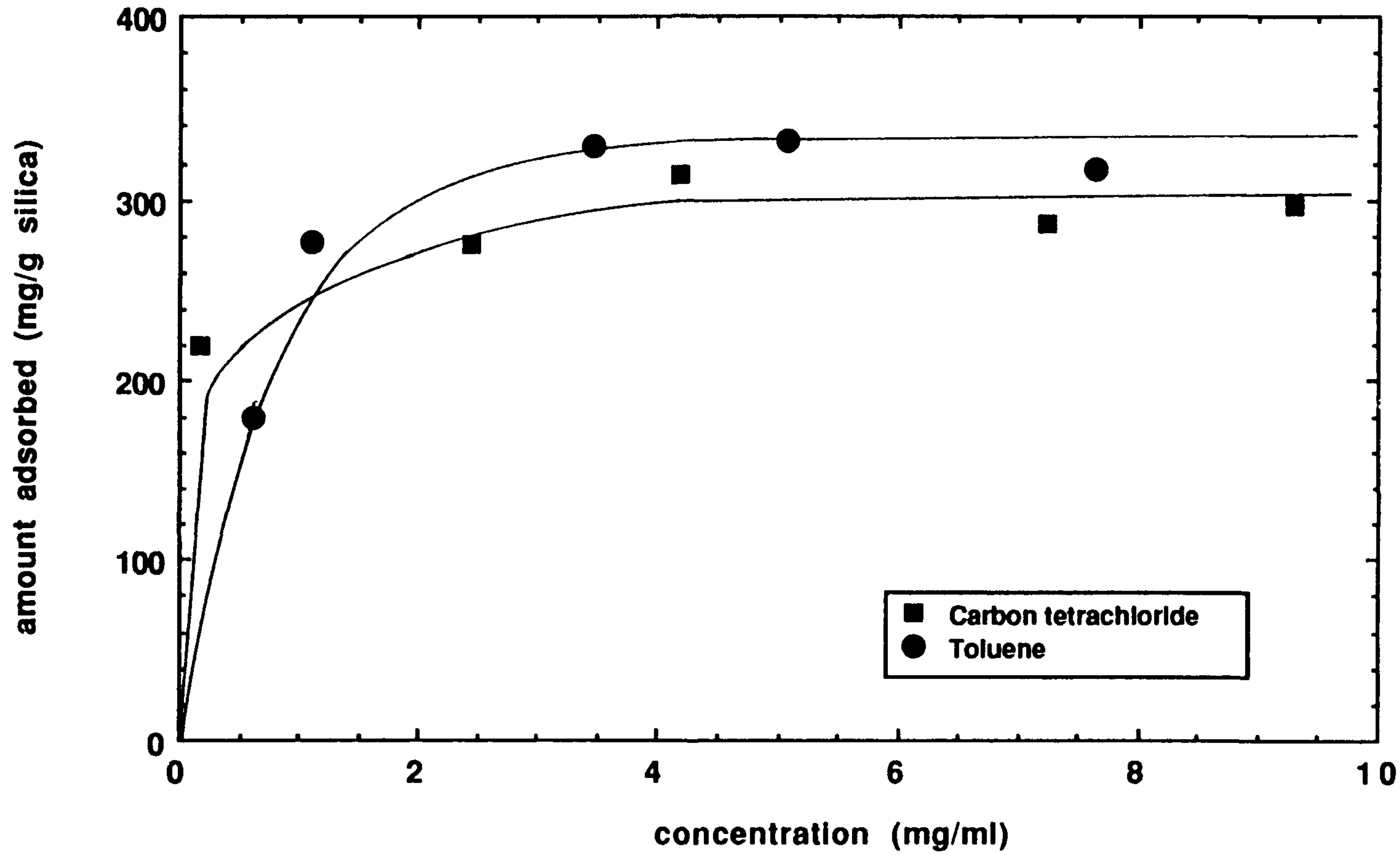
Figure Captions

Figure 1. Adsorption isotherms of VPS-7 on silica in carbon tetrachloride and toluene.

Figure 2. Solution ^{2}H relaxation times for labelled polystyrene (DS) as a function of concentration (g/100 ml) and temperature in CCl_4.

Figure 3. Carbon-13 spectrum of VPSDS adsorbed on silica and swollen with CCl_4/CH_3OH. The non-overlapping resonances for 2-vinylpyridine and CCl_4 are marked V and C, respectively.

Figure 4. Solution ^{2}H relaxation times for the labelled block copolymer (VPSDS) as a function of concentration (g/100 ml) and temperature in CCl_4/CH_3OH.



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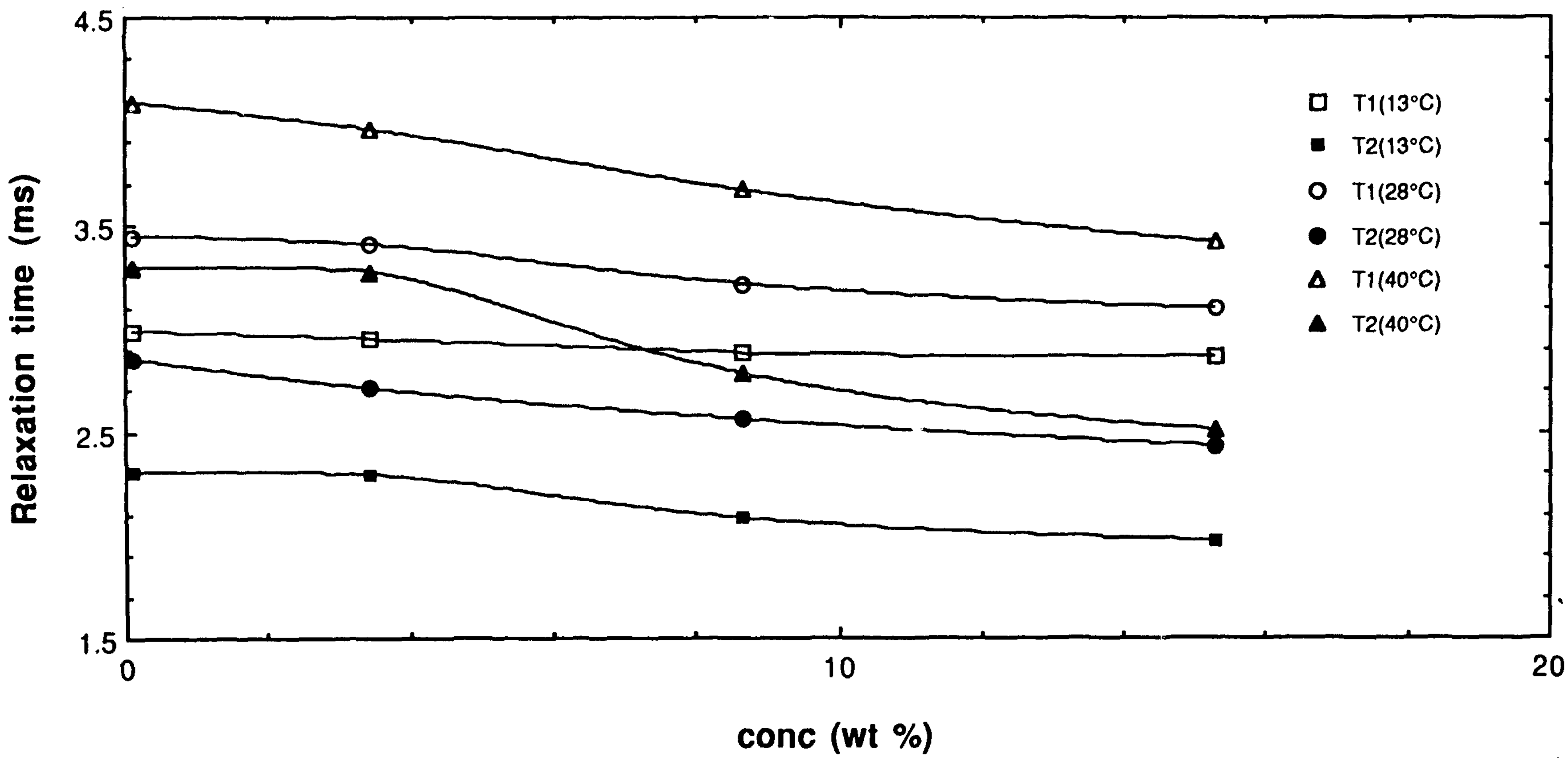

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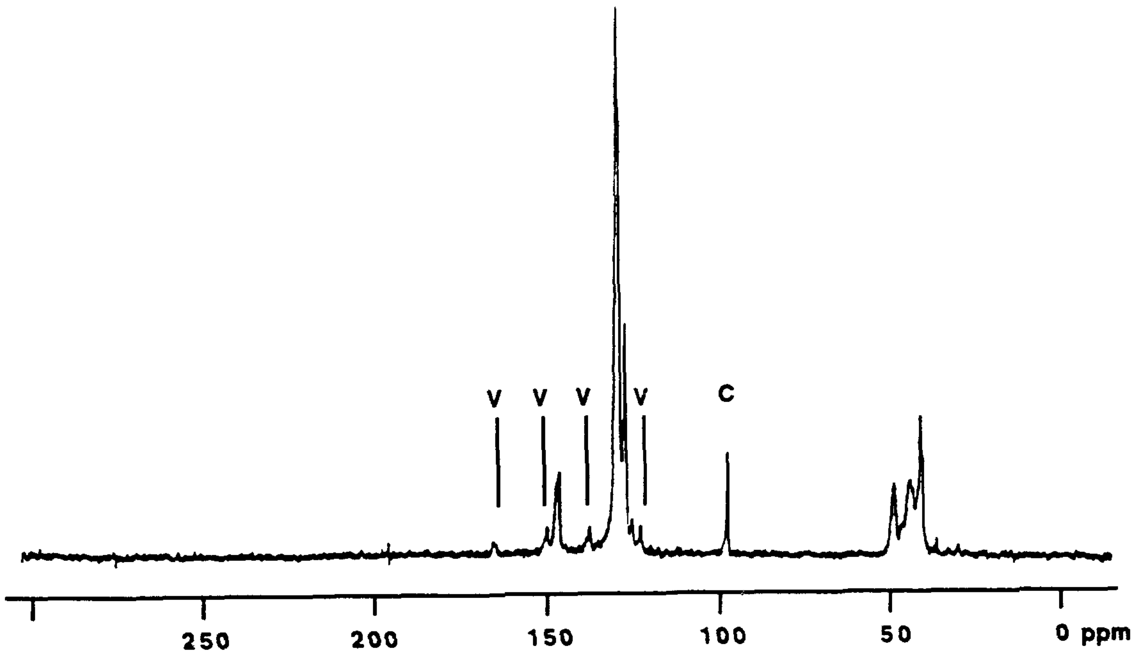

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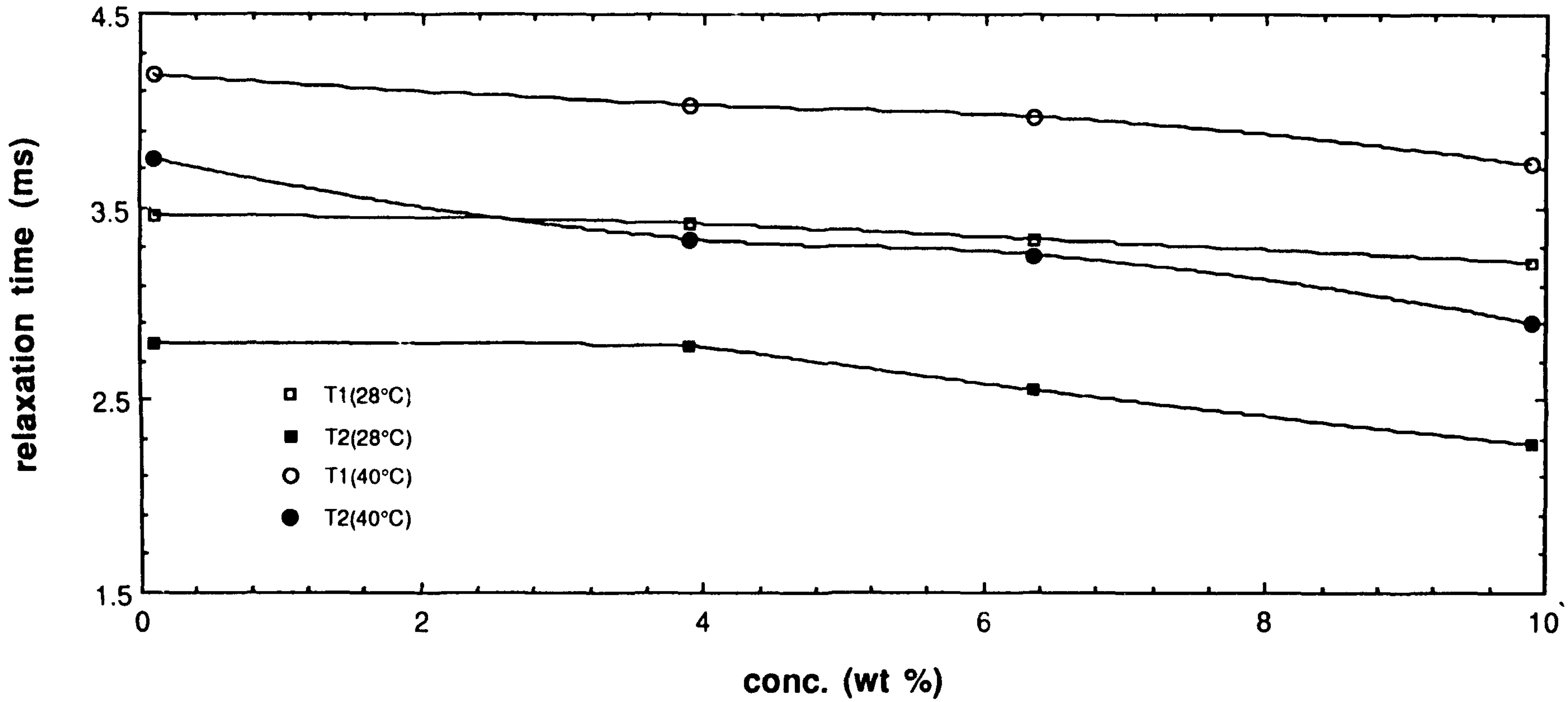

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